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Author(s):

John L Lyman and W. Dale Breshears

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John L. Lyman¹ and W. Dale Breshears

Los Alamos National Laboratory

E-mail: lyman@lanl.gov

Abstract

We have performed laser absorptions experiments designed to select the best two CO₂ laser frequencies for zirconium isotope separation using the molecule zirconium tertaborodeuteride. The experiments were performed in the pulsed recirculating loop used previously for uranium isotope separation. The frequencies selected were 895 cm⁻¹ for the second frequency and one of several frequencies in the strong infrared absorption band centered at 918 cm⁻¹. Subsequent enrichment experiments showed that no isotopic enrichment occurred. We conclude that chemical reaction occurring after photolysis scrambled the isotopic identity of the photoproduct.

Introduction

The zirconium isotope separation program at Los Alamos in 1983 and lasted for less than one year. The objective was to demonstrate that one could use one or two carbon dioxide laser frequencies to separate zirconium isotopes by multiple photon dissociation of the molecule zirconium tetraborodeuteride (ZBD), $\text{Zr}(\text{BD}_4)_4$. That species is one the few volatile compounds of zirconium and it absorbs carbon dioxide laser radiation.

Westinghouse funded the program, and we made reports to them. Our research was also directed by and monitored by Westinghouse representatives. Most of what is in this report was included in monthly progress reports to Westinghouse. Unfortunately, I have not been able to find many of those reports, nor was I able to locate a final report.

The proposal we made to Westinghouse was to use a procedure similar to the one that had been used for the uranium molecular laser isotope separation (MLIS) at Los Alamos. We had available infrared spectra of the ZBD species and noted that it had a strong infrared absorption band in the $11\text{ }\mu\text{m}$ spectral region. A preliminary analysis of the assignment of the band indicated that it would have a zirconium isotope shift. We planned to cool a dilute mixture of ZBD with nitrogen by supersonic expansion in the Laval nozzle of the pulsed recirculating loop that had been used for uranium enrichment. A first infrared laser would excite the molecule in an isotopically selective manner. A second laser would then dissociate the vibrationally excited molecules by infrared multiple photon dissociation. The reaction products were expected to be BD_3 and $\text{ZrD}(\text{BD}_3)_3$. The latter species would condense to solid, nonvolatile clusters and be collected from the flow in the PRL by a sonic impactor collector that had been designed for the uranium program. If all went well this collected product would be enriched in the desired zirconium isotope.

Much of this report involves the measurement of the absorption of the first and second laser frequencies. This information was used to select the appropriate infrared laser frequencies and intensities. We also report the successes (or lack of success) of this research project.

Experimental Procedure

The procedure we used was to cool a dilute mixture of ZBD in nitrogen by supersonic expansion in a Laval nozzle. The nozzle was part of a pulsed recirculating loop (PRL) that had been used for uranium isotope separation experiments. The pulsed nozzle dropped the temperature to about 100 K, which was intended to simplify the infrared spectrum and enhance isotopic selectivity. Jensen, *et al.* [1] gives a more complete description of the PRL and its use for uranium isotope separation. Figure 1 show a representation of that nozzle. It was taken from Reference 1. The second infrared laser replaced the labeled UV laser. The fluorescence signal and dye laser was not used. However, we used a visible HeNe laser at that position to obtain the laser Schlieren signals for determining the amount of infrared laser energy absorbed by the ZBD.

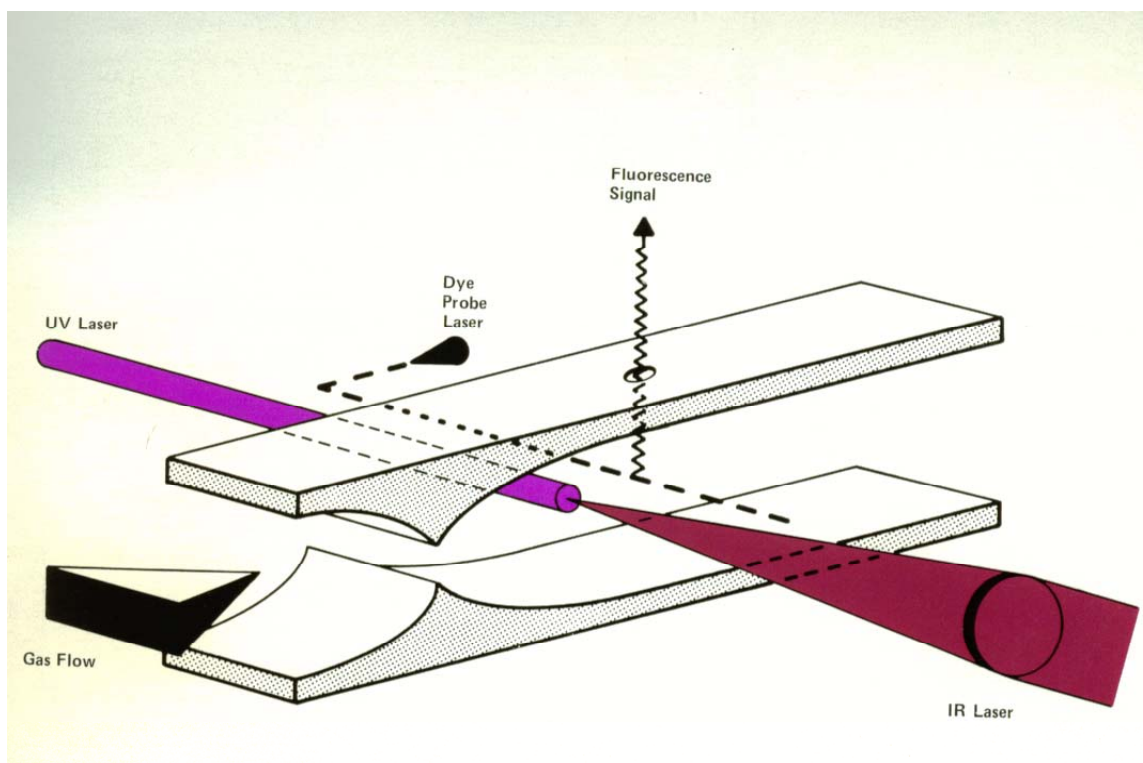


Figure 1. Schematic diagram of the nozzle used for zirconium isotope separation experiments. See text for changes made in the zirconium experiments.

The laser Schlieren experiments were arranged such the HeNe laser beam was about two centimeters after the infrared lasers. After the laser pulse or pulses the vibrational energy would relax to thermal energy and expand the gas. This expansion would result in a change of refractive index, which in turn would deflect the HeNe laser beam. We detected the deflection by directing the beam to a knife-edge and the transmitted part of the beam to a photomultiplier. As the infrared laser heated region passed through the HeNe beam the signal to the photomultiplier would first rise to a peak, then fall through the initial level to make a negative peak, and finally rise to the initial signal level. This resulted in a signal similar to the derivative of a Gaussian peak. We processed this signal by numerically integrating it. The result was peak whose integral was proportional to the amount of absorbed laser energy.

The ZBD was synthesized by chemist at Westinghouse and transported to us. The material is a clear solid with sufficient vapor pressure to be a gas at reasonable densities in the PRL. It was mixed with nitrogen in the loop. The ZBD was a minor component and nitrogen dominated the aerodynamic properties of the gas mixture.

In the infrared photolysis experiments the nonvolatile zirconium-containing fragment condensed to small particles as the gas flowed into a large-volume section of the loop called a "surge tank." After the gas flowed through a sonic impactor (Figure 2), which had also been designed for the uranium experiments. The sonic impactor accelerated the gas by constricting the flow through a series of small holes. The high-speed particles of photolysis product then impacted a collector plate. After an enrichment run, where the

gas mixture was photolyzed with the infrared lasers, the collection plate was removed. Researchers in the laboratory's analytical chemistry group measured the extent of zirconium isotope enrichment in the collected product.

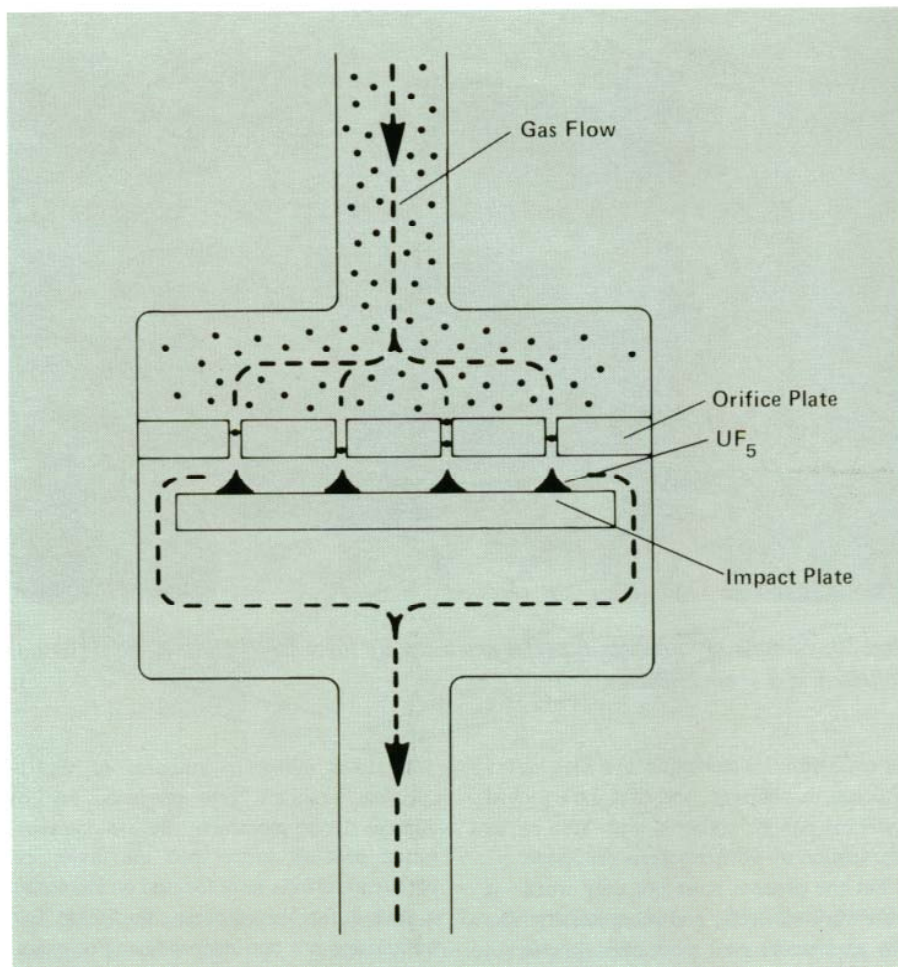


Figure 2. Sonic impactor collector used in the zirconium isotope separation experiments. The figure is from Reference 1 and was designed for uranium enrichment.

The infrared lasers used in the experiments were commercial pulsed CO_2 lasers made by Lumonix Corp. One of the lasers used carbon-13 CO_2 . This was necessary to obtain the longer wavelengths used for photolysis of ZBD.

Infrared absorption measurements

We have completed the measurements of two-frequency absorption measurements on the 10- μm band of flow-cooled zirconium tetraborodeuteride (ZBD). Our goal was to measure the effect of vibrational excitation by a first laser on absorption at a second frequency. We used laser-Schlieren technique to measure the amount of energy absorbed.

The first laser in all two-frequency experiments was the 10P46 line of $^{12}\text{CO}_2$ at 918.72 cm^{-1} . The second laser was also a $^{12}\text{CO}_2$ laser for all frequencies above 925 cm^{-1} , but a

$^{13}\text{CO}_2$ laser for all, frequencies below 925 cm^{-1} . The beam area was about 3 mm^2 for the first frequency and about 4 mm^2 for the second.

Unless otherwise noted the delay time between the two lasers was $1.0\text{ }\mu\text{s}$. We adjusted all data for changes in the ZBD concentration during the course of the experiments.

In changing the laser systems to make the lower-frequency measurements, we changed the beam sizes and shapes somewhat. We tried to minimize these changes.

In the course of performing these experiments we made many measurements at the frequency of the first laser, the 10P46 line. Figure 3 shows the results of all of these measurements. Each point on the graph is the result of a single measurement at a single frequency, 918.72 cm^{-1} . The figure gives an indication of the scatter in the absorption measurements. Each set of data has a different symbol. We performed each set of measurements over a short time period (about thirty minutes.) Note that the scatter within a single set is less than among the sets. Our major source of error over long time periods (days) was in the measurement of the laser pulse energies, that is, in the calibration of the detectors. Minor movement of the laser beams also contributed to that error. These data also show the dependence on the $2/3$ power of the laser energy that we observed in earlier experiments with this and other species. [2] The slope of the solid line in Figure 3 is $2/3$.

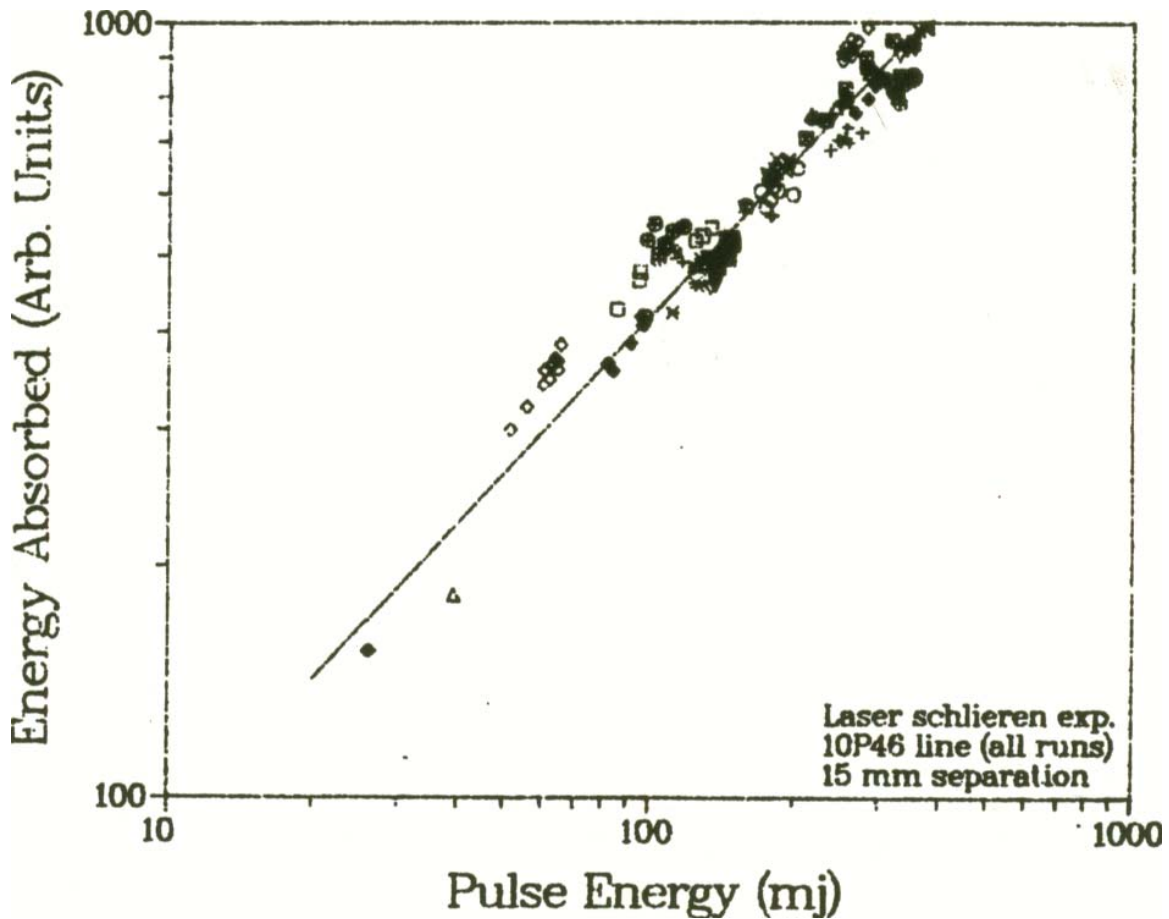


Figure 3. Energy absorbed (as measured by the laser Schlieren technique) versus the pulse energy at the frequency of the 10P46 $^{12}\text{CO}_2$ laser line. The separation between the pulsed laser and the Schlieren probe was 15 mm.

Figure 4 shows the results of the absorption measurements with a single laser over a range of frequencies. The actual, pulse energies were between 90 and 140 mJ for frequencies below 925 cm^{-1} and between 50 and 400 mJ at the higher frequencies. For the frequencies with two data points, one point is in the region of 100 mJ and the other is near 300 mJ. We adjusted all results to 200 mJ by assuming that the absorption increased with the $2/3$ power of the laser energy (as in Figure 3). The points in the figure are all relative to absorption at the peak of the absorption (918.72 cm^{-1}). We used a different set of data for this adjustment for each side of the band.

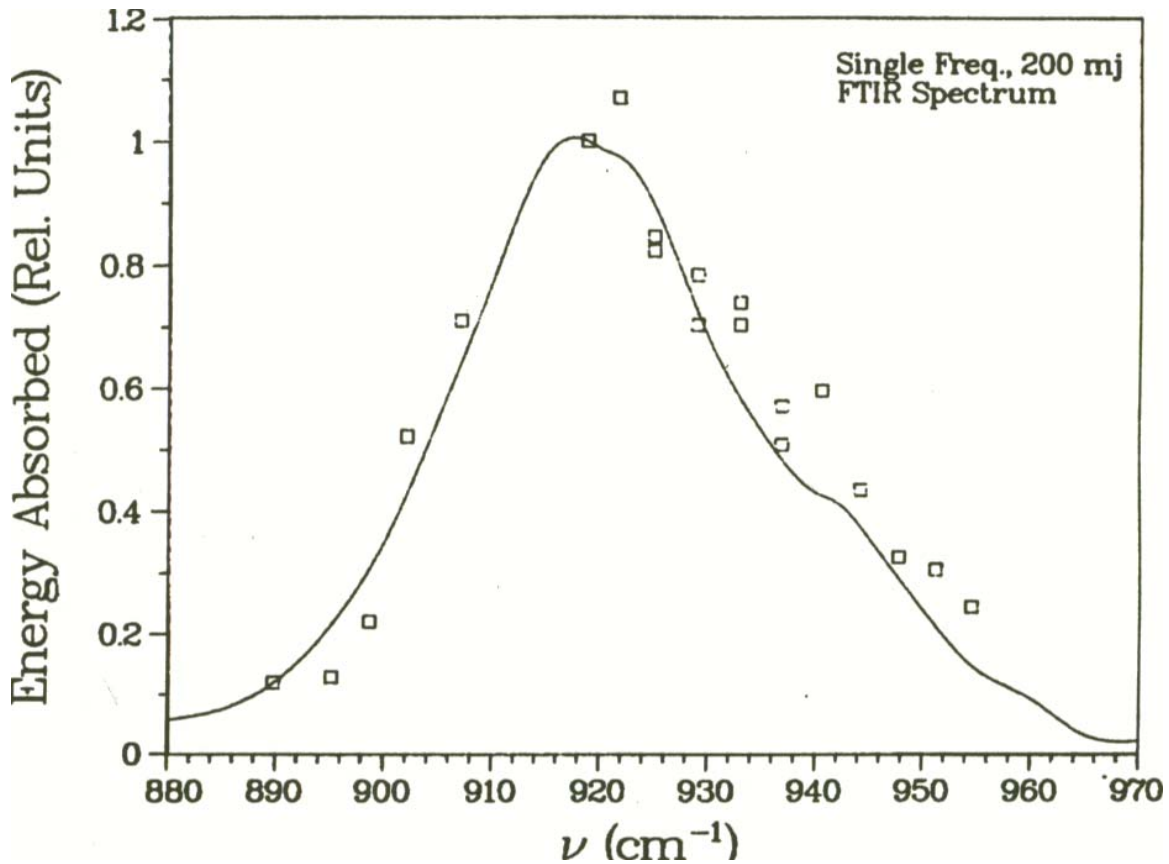


Figure 4. Absorbed energy versus frequency with no first laser. All measurements were adjusted to 200 mJ by assuming the 2/3 slope in Figure 3. The solid curve is the FTIR spectrum of ZBD at room temperature.

The solid line in the figure is the room-temperature spectrum of ZBD. Note that the absorption follows the spectrum quite closely. We may be seeing some effect of cooling. The points below 900 cm^{-1} appear to be lower than the room-temperature spectrum. (The spectrum is narrower at lower temperature.) The lower temperature also appears to enhance the shoulder at 942 cm^{-1} .

Figure 5 shows the enhancement produced by the first laser. The quantity plotted is just

$$\eta^*/\eta^1 = [A_t(E_1, E_2) - A_1(E_1)]/A_2(E_2)$$

where η^* is the number of laser quanta absorbed per molecule following excitation by the first laser. η^1 is the number of quanta absorbed without the first laser. $A_t(E_1, E_2)$ is the total energy absorbed by the gas at both frequencies at the pulse energies E_1 and E_2 . $A_1(E_1)$ is the energy absorbed from the first laser pulse, and $A_2(E_2)$ is the same for the second laser. The quantities A_t , A_1 , and A_2 are the areas of the expansion transient measured by the laser Schlieren technique.

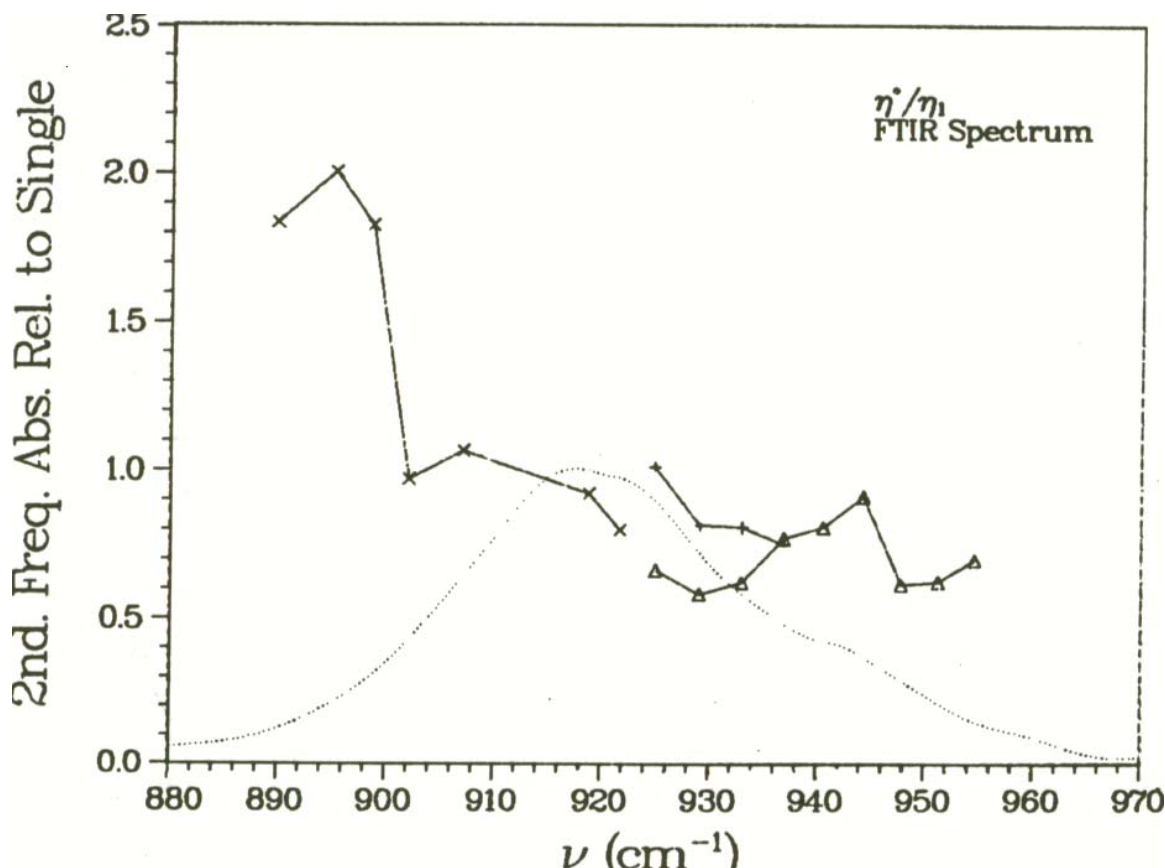


Figure 5. Absorbed energy of the second laser relative to absorption at the same frequency and pulse energy in the absence of a first laser pulse.

If the absorption at the first frequency had not altered the absorption at the second frequency, then all the points would have been at 1.0 for all second frequencies. As expected, the vibrational excitation enhances absorption at the low frequency extreme of the band. The vibrational excitation also appears to produce a minor, but still enhanced, peak near the shoulder at 942 cm^{-1} .

The triangles "Δ" are for the high energies (150-400 mJ) with the $^{12}\text{CO}_2$ laser. The plus symbols "+" are for the low energies (50-150 mJ) with that laser. The X symbols are for the $^{13}\text{CO}_2$ laser pulses with energies in the range 100-140 mJ. The dotted curve is the FTIR spectrum of ZBD.

To get a better picture of the excited state spectrum, we took the product of the points in Figure 4 and Figure 5. Figure 6 shows that spectrum. Note that the major effect of vibrational excitation is to shift the spectrum to lower frequencies and enhance the absorption near the shoulder at 943 cm^{-1} .

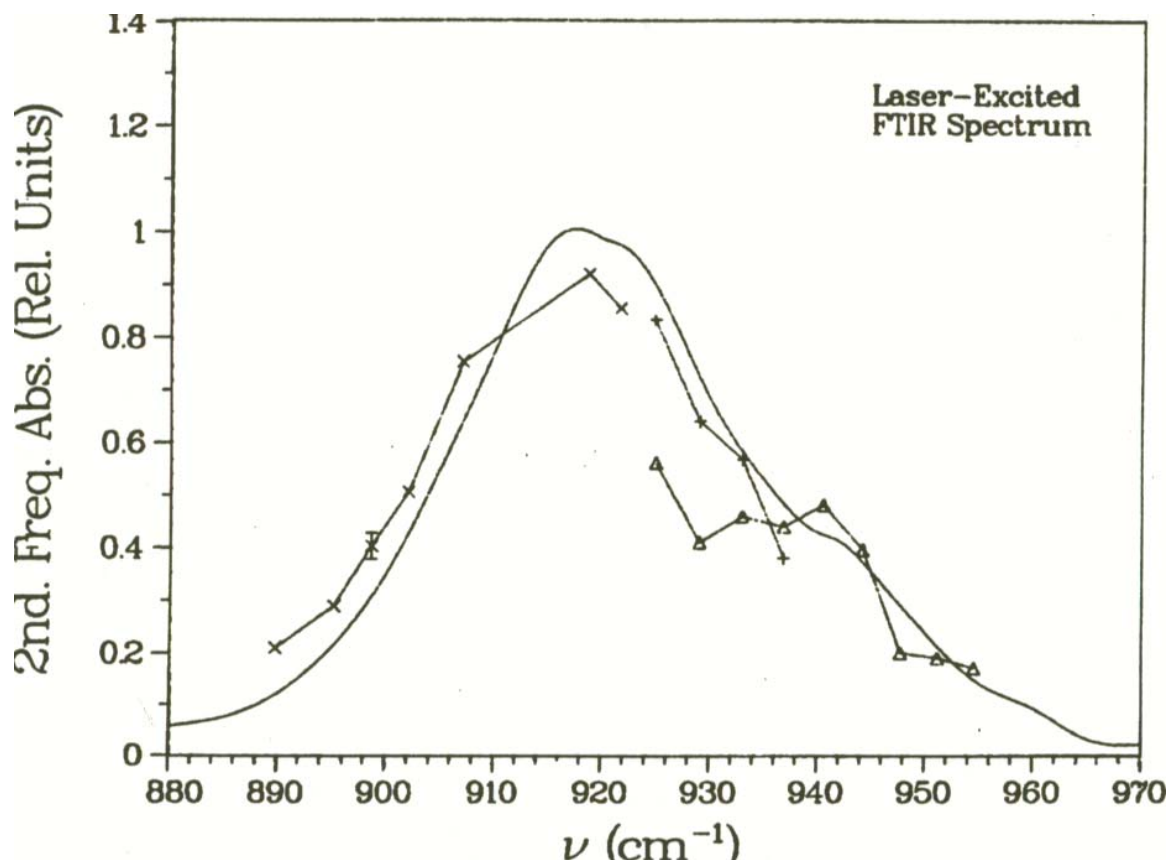


Figure 6. Derived spectrum of ZBD after excitation with the first laser. The text explains the meaning of the different symbols.

We conclude from these experiments that the best frequencies for a second laser are near 895 cm^{-1} . This region is where the $^{13}\text{CO}_2$ laser operates best.

We performed an additional experiment to determine the effect of delay time between the first and second laser pulse. In these experiments the first frequency was 918.72 cm^{-1} , and the second was 898.65 cm^{-1} . We varied the delay time between -1.5 and $2.0\text{ }\mu\text{s}$. For delay times in excess of $2.0\text{ }\mu\text{s}$ the gas movement begins to alter the beam overlap. Figure 7 shows the result of this experiment. This figure indicates that the best delay time is about $1.5\text{ }\mu\text{s}$.

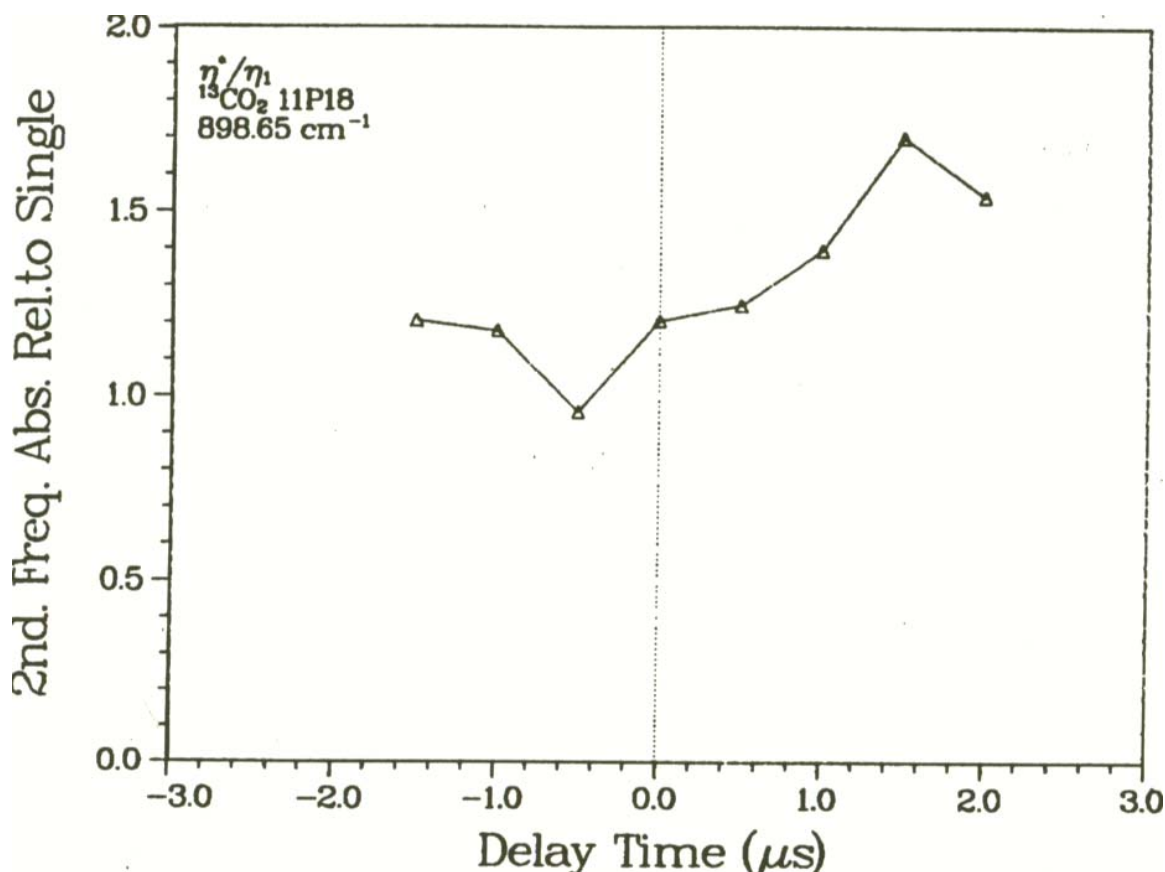


Figure 7. Enhanced absorption of the second laser (absorbed energy relative to absorption with no first laser) versus delay time between the two laser pulses.

Attempts at isotope separation

Zirconium had five naturally occurring isotopes. They are atomic masses 90, 91, 92, 94 and 96. This is sufficient spread to have hope of seeing enrichment in either the light or the heavy isotopes.

After completion of the absorption measurements we were ready to check the isotopic selectivity of the infrared photolysis process. We did many experiments where we used only a single CO₂ laser. We used a number of frequencies across the absorption band (Figure 4). The collected solid material was then analyzed with the high precision mass spectrometers in the analytical chemistry group at the Los Alamos National Laboratory. The analysis showed that the zirconium isotope distribution in the product was completely natural to three significant figures.

An earlier review had shown that two frequencies are superior to one. [3] Often no enrichment occurs for isotopes of heavy atoms without a second frequency. The reason for doing the two-frequency absorption experiment described above was to be able to select the best two frequencies for isotope separation.

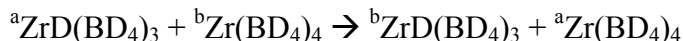
We repeated the enrichment experiments with two frequencies. We varied the first frequency within the absorption band (Figure 4) and set the second frequency at what we had earlier decided to be the optimum, 895 cm⁻¹. We again performed many experiments and had the collected products analyzed. The results were again the same. The zirconium

isotope distribution was natural to three significant figures. We observed absolutely no isotope enrichment.

On considering what we had done in the experiments we decided from the spectroscopic and absorption experiments that the two-frequency excitation at low temperatures should have resulted in an isotopically selective reaction of the type



We read, at the time, that the reaction products of species such as ZBD are very labile. That is, exchange reaction occur readily, such as



where the *a* and *b* label different zirconium isotopes. We believe that the photochemistry was isotopically selective, but that the exchange reactions complete scrambled the isotopic distribution in the collected products.

Conclusions

We performed many absorption experiments to select the best time delay and laser frequencies for isotopically selective dissociation of ZBD and selected the optimum values. Experiments performed with optimum and near optimum conditions resulted in collected photoproduct. Isotopic analysis of the collected photoproduct was analyzed for isotopic distribution. In all of many experiments the isotopic distribution in the collected product was natural. No isotope enrichment occurred. We concluded that chemical reactions after photolysis scrambled the initially enriched photoproduct back to a natural isotopic distribution.

Acknowledgements

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